PHYSICAL REVIEW B VOLUME 17, NUMBER 10 15 MAY 1978

Diffuse neutron scattering in Nb-Zr alloys

N. Wakabayashi
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 18 November 1977)

The diffuse scattering of neutrons has been observed in the alloys $Nb_{0.95}Zr_{0.05}$ and $Nb_{0.88}Zr_{0.12}$ along the [111] direction around various reciprocal-lattice points. The intensity profiles were interpreted on the basis of the scattering cross section due to the lattice distortions caused by the substitutional impurity atoms. The observed peak near $(3/4)\langle 111\rangle$ can be related to the longitudinal phonon dispersion curve which has a local minimum near this wave vector.

I. INTRODUCTION

$Nb_{1-x}Zr_x$ alloys have the bcc structure for Zr concentrations less than 15 at. % and the superconducting transition temperature T_c increases slightly (from 9 to 11 K) as x increases in this concentration range. For greater Zr concentrations, the alloys seem to have a mixed bcc–diffuse-ω-phase at low temperatures.[1] The Bragg reflections characteristic of the ω phase correspond to $\frac{2}{3}\langle 111\rangle$ which is the position of the pronounced minimum in the frequency of the longitudinal-phonon branch. Slow-neutron-scattering studies have been reported on the static and dynamic states of atoms in such alloys. These reports include the diffuse-scattering experiment associated with the bcc-to-ω-phase transition[2] and the anomalous phonon branch in the high-temperature bcc phase.[3] The diffuse-scattering intensity pattern was explained by assuming the existence of small regions of hexagonal structure (ω phase) in the bcc structure.[1] In addition, anomalous phonons in the high-temperature bcc phase were interpreted as a dynamic modulation of staticlike short-range order.[3] In contrast to the tendency toward phase instability in Nb-Zr alloys, the structure of Nb alloyed with Mo remains bcc and such alloys show a marked decrease in the superconducting transition temperature as the Mo concentration is increased. Also, the frequency of the $\frac{2}{3}\langle 111\rangle$ longitudinal-phonon branch increases with the Mo concentration,[4] indicating the system becomes more stable.

However, a recent neutron-scattering experiment[5] shows that the phonons observed for $Nb_{0.95}Zr_{0.05}$ and $Nb_{0.88}Zr_{0.12}$ are well defined and dispersion curves do not exhibit significant decreases in the frequencies of longitudinal modes near $\frac{2}{3}\langle 111\rangle$ where the frequency is at a minimum. The present report deals with the diffuse scattering near this wave vector observed for the Nb-Zr alloys with compositions mentioned above. A possible origin of the diffuse scattering will be proposed.

II. EXPERIMENT AND RESULTS

The experiment was carried out on the HB-4A triple-axis spectrometer at the High Flux Isotope Reactor. A Be(101) plane was used as a monochromator and most of the measurements were made with a Ge(111) plane as the analyzer. Thus, contaminations due to neutrons with energies cor-

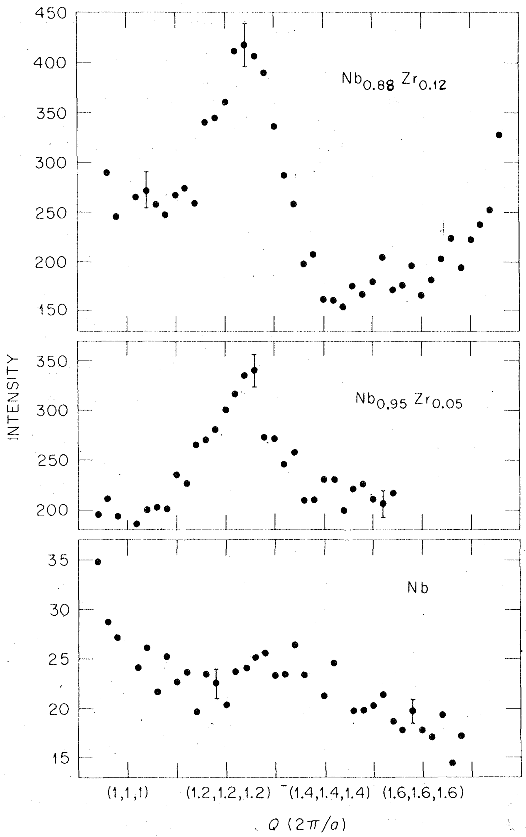

FIG. 1. Diffuse-scattering peaks observed in niobium and niobium-zirconium alloys. Intensities are normalized to that of the LA (0.200) phonon. Note the different intensity scale for niobium.

responding to the second- and third-order reflections were almost negligible. The incident neutron energy of 51 meV was used to cover a large region in reciprocal space. The alloy samples were the same as used for phonon-dispersion-curve measurements.[5] Scans with zero energy transfer (elastic scans) were carried out mainly along the ⟨111⟩ direction from various reciprocal lattice points. Figure 1 shows the elastic scans in the [111] direction from (1,1,1) to (1.8,1.8,1.8) for Nb, $Nb_{0.95}Zr_{0.05}$, and $Nb_{0.88}Zr_{0.12}$. In order to take into account the difference in the sample sizes, the counts are normalized to the relative intensity of the LA phonon at (0.2,0,0) (in units of $2\pi/a$, where a is the lattice constant 3.3 Å) which seems to be unaffected by alloying. The rise in the count rate near (1,1,1) is due to the high background at low scattering angles. The scan for $Nb_{0.95}Zr_{0.05}$ does not show this background effect because of its large sample size and, hence, good peak-to-background ratio. The q resolution of the instrument was estimated from scans around Bragg reflections and found to be about 0.01 in the present unit. The peak widths for the two alloys seem to be identical. The scattering intensity increases with the Zr concentration, and it peaks at about $\frac{3}{4}(1,1,1)$ for alloys, whereas an extremely weak maximum seems to exist near $\frac{2}{3}(1,1,1)$ for pure Nb. The x-ray studies by Chang and Collela[6] did not detect the diffuse peak in pure Nb. Similar scans from several reciprocal lattice points were carried out and some of the results for $Nb_{0.88}Zr_{0.12}$ are shown in Fig. 2(a) which includes the scan of Fig. 1. Figure 2(b) shows the lines in reciprocal space corresponding to the scans in Fig. 2(a). Several constant-Q scans for wave vectors near the diffuse peak were performed and examples of the results are shown in Fig. 3. Scans were made with the incident energy fixed at 51 meV. The energy widths of both the diffuse and phonon peaks are those expected from the resolution function of the instrument. Consequently, the intrinsic energy widths, if any, could not be observed.

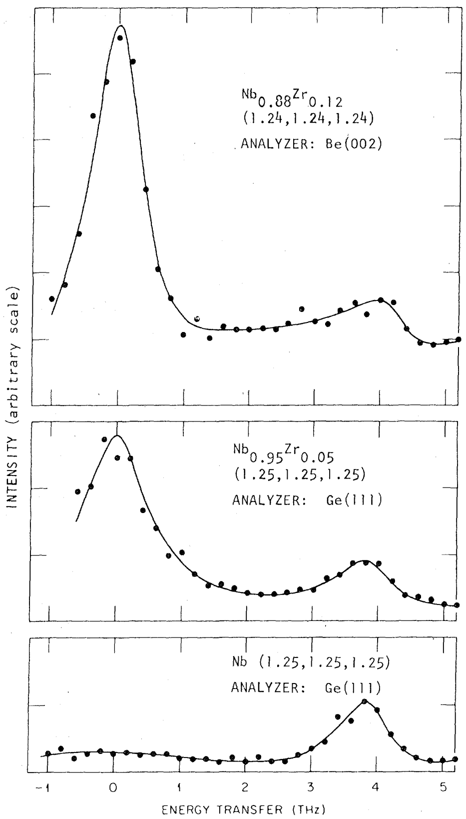

FIG. 3. Constant-Q scans near the intensity maxima.

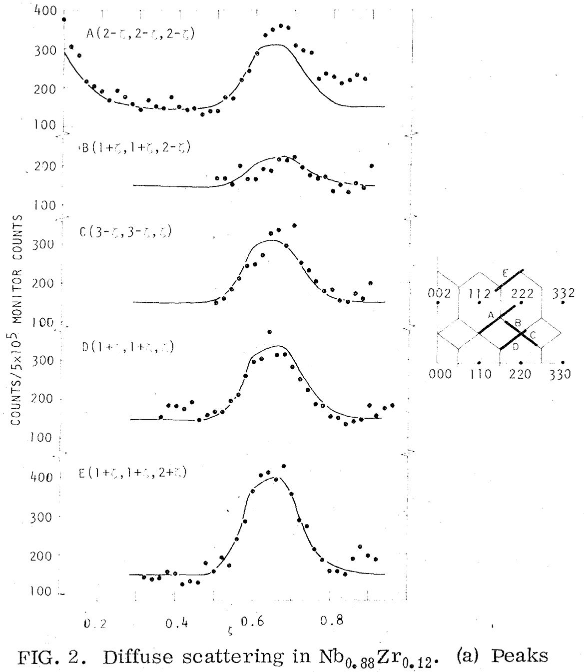

FIG. 2. Diffuse scattering in $Nb_{0.88}Zr_{0.12}$. (a) Peaks observed along various ⟨111⟩ directions. Solid lines are calculated intensities. Same background counts and scaling factor are used for all the scans. (b) Paths in the reciprocal space corresponding to the scans in (a).

III. DISCUSSION

Information about the nature of the atomic displacements giving rise to the diffuse scattering may be obtained from the position and width of the diffuse peak and also from the Q dependence of the scattering intensity. In the present observation, the peak position q_0 is very close to $\frac{3}{4}(1,1,1)$ which is significantly different from the ω-phase peak position $\frac{2}{3}(1,1,1)$. If the peak position is exactly $\frac{3}{4}(1,1,1)$, the displacement is commensurate with the host lattice and the periodicity is $8d$ where d is the distance between the planes of the atoms perpendicular to the $(1,1,1)$ direction, or $d=a/2\sqrt{3}$. However, the observed peak width $\Delta q = \sqrt{3}\,(2\pi/a)\times 0.14$ suggests that the size of the region in which displacements are coherent is represented approximately by 14 planes. Since the periodicity of the microcrystal is comparable to its size, a picture in which the microcrystalline regions are assumed to be randomly embedded in the bcc host crystal may not be a suitable description. Furthermore, the phonons near q_0 are not softened significantly by alloying, and, as Fig. 3 shows, the diffuse-scattering peak does not seem to be due to the condensation of a soft longitudinal phonon in the $(1,1,1)$ direction. Instead, it may be interpreted as a scattering due to a lattice distortion caused by the presence of impurity Zr atoms, as in the case of Huang scattering.[7] According to the model described in the Appendix, the scattering intensity for q in the $(1,1,1)$ direction is approximately proportional to

$$c[\vec{\mathrm{Q}}\cdot\vec{\mathrm{e}}(\vec{\mathrm{q}},L)]^2 e^{-\alpha^2[\vec{\mathrm{Q}}\cdot\vec{\mathrm{e}}(\vec{\mathrm{q}},L)]^2}W(\vec{\mathrm{q}}), \tag{1}$$

with

$$W(q)=\sin^2\pi\zeta\cos^2\pi\zeta/\omega_L^4(q), \tag{2}$$

where c is the impurity concentration, $\vec{\mathrm{Q}}=\vec{\mathrm{q}}+\vec{\tau}$, $\vec{\tau}$ is the reciprocal-lattice vector, $\vec{\mathrm{q}}=\zeta(2\pi/a)\vec{\mathrm{e}}(\vec{\mathrm{q}},L)$, and $\omega_L(\vec{\mathrm{q}})$ is the frequency of the longitudinal phonon for wave vector $\vec{\mathrm{q}}$. $\vec{\mathrm{e}}(\vec{\mathrm{q}},L)$ is the eigenvector of the longitudinal phonon in the $(1,1,1)$ direction, namely, $(1/\sqrt{3})(1,1,1)$or its equivalent. α^2 is, in principle, determined by the amplitude of the atomic displacement, but in the present analysis it is regarded as a parameter. The peak intensity at $q=q_0$ is determined by the first three factors in Eq. (1). The relative intensities of the observed peaks and the intensities calculated with $\alpha^2 = 0.023(2\pi/a)^2$ are compared in Table I. The q dependence of the intensity, on the other hand, is mainly determined by $W(q)$.[8] The lines in Fig. 2(a) represent the intensities calculated from Eq. (1) with the phonon frequency of Nb. The same background count and scaling factor were used for all the scans. Although the factor $1/\omega^4$ has a maximum near $\zeta=\frac{2}{3}$ or $\vec{\mathrm{q}}=\frac{2}{3}(1,1,1)(2\pi/a)$, the factor $\sin^2\pi\zeta\cos^2\pi\zeta$ is largest at $\zeta=0.2$ and 0.8. As a result, $W(q)$ has a peak at $\zeta\cong\frac{3}{4}$. Also, the intensity diverges around the Bragg points as $1/\zeta^2$ corresponding to the conventional Huang scattering. Diffuse scattering from $Zr_{0.8}Nb_{0.2}$ observed by Keating and LaPlaca[2] showed peaks whose position is $0.7(1,1,1)$ rather than $\frac{3}{4}(1,1,1)$ and regions of high intensity near the Bragg points of the bcc structure were found. The scattering in the Zr-rich alloy is certainly related to the incipient ω transition. However, within the present picture the difference in the peak positions for two different ranges of the impurity concentration may be considered to be due to the breakdown of the assumption that the total atomic displacement due to impurities can be expressed as a linear superposition of the displacement due to each impurity atom for higher impurity concentrations. Also, the interatomic forces must be modified considerably for alloys with high impurity concentrations.

TABLE I. Relative intensity of diffuse scattering.

	A	B	C	D	E
Observed	1	0.42	1	1.17	1.38
Calculated	1	0.39	1	1.06	1.36

IV. CONCLUSIONS

Similar phenomena are expected to exist in alloys with large lattice distortions. Very preliminary measurements on Ta containing 2-at.% deuterium as interstitial impurities indicate the existence of rather weak diffuse scattering near $\frac{5}{4}(1,1,1)=\vec{\tau}-\frac{3}{4}(1,1,1)$, where $\vec{\tau}=(2,2,2)$. Also, diffuse-scattering peaks which are several orders of magnitude stronger than those for Nb(Zr) have been observed for Nb containing 3.6-at.% oxygen atoms with a smaller q width along various $\langle 111\rangle$ directions. However, there may be short-range order of oxygen atoms in this system[9] although the large changes in the phonon frequencies observed in such a system[10] suggest that oxygen atoms are probably rather uniformly distributed in the crystal. Further investigation will be undertaken to check the validity of the model discussed in this report.

ACKNOWLEDGMENTS

The author is grateful to J.G. Traylor and F. A. Schmidt for preparing the samples. He also wishes to thank H. G. Smith for many helpful discussions and for critical reading of the manuscript. This research was sponsored by the Division of Materials Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with the Union Carbide Corp.

APPENDIX

In this Appendix the expression for the elastic-scattering cross section of neutrons due to impurities is derived in terms of the lattice Green's function and the change in the interatomic potentials. The atomic position is written $\vec{r}(l) = \vec{r}^0(l) + \vec{\Delta}(l)$, where $\vec{r}^0(l)$ is the equilibrium position of the lth atom in a pure crystal. The energy of the entire crystal with an impurity atom at the origin is expressed $\Psi = \Phi + \Lambda$, where Φ is the potential energy without the impurity and Λ is the change in the energy. The atomic displacement $\vec{\Delta}(l)$ due to the impurity is assumed to be small and the energy functions expanded in terms of the $\vec{\Delta}(l)$'s are

$$\Psi = \Phi_0 + \frac{1}{2} \sum_{\substack{ll' \\ \alpha\beta}} \Phi_{\alpha\beta}(ll')\Delta_\alpha(l)\Delta_\beta(l') + \Lambda_0$$

$$+ \sum_{l\alpha} \Lambda_\alpha(l)\Delta_\alpha(l) + \cdots ,$$

where $\Lambda_\alpha(l) = \partial\Lambda/\partial r_\alpha^0(l)$, $\alpha = x, y$, or z, and $\Phi_{\alpha\beta}(ll')$ is the interatomic force constant in the pure crystal. The equilibrium condition, $\partial\Psi/\partial\Delta_\alpha(l) = 0$ for all (l, α), gives

$$\sum_{l'\beta} \Phi_{\alpha\beta}(ll')\Delta_\beta(l') + \Lambda_\alpha(l) = 0 .$$

Thus, we have

$$\Delta_\alpha(l) = -\sum_{l'\beta} G_{\alpha\beta}(ll')\Lambda_\beta(l') ,$$

where $G_{\alpha\beta}$ is the lattice Green's function of the pure crystal.

The neutron elastic-scattering cross section can be written, in terms of the structure factor $F(\vec{Q}) = \sum_l e^{i\vec{Q}\cdot\vec{r}(l)}$, as

$$|F(\vec{Q})|^2 = \sum_{ll'} e^{i\vec{Q}\cdot[\vec{r}(l)-\vec{r}(l')]} ,$$

since the scattering amplitudes for Nb and Zr are almost identical. For $\vec{Q} = \vec{\tau} + \vec{q}$,

$$|F(\vec{Q})|^2 = \sum_{\substack{ll' \\ \alpha\beta}} e^{i\vec{Q}\cdot[\vec{r}^0(l)-\vec{r}^0(l')]} Q_\alpha Q_\beta \Delta_\alpha(l)\Delta_\beta(l') + \cdots$$

$$= \sum_{\substack{ll' \\ \alpha\beta}} e^{i\vec{Q}\cdot[\vec{r}^0(l)-\vec{r}^0(l')]} Q_\alpha Q_\beta \sum_{\substack{l_1 l_2 \\ \gamma\delta}} G_{\alpha\gamma}(ll_1)G_{\beta\gamma}(l'l_2)\Lambda_\gamma(l_1)\Lambda_\delta(l_2) + \cdots$$

$$= \sum_{\alpha\beta} Q_\alpha Q_\beta \sum_{\gamma\delta} G_{\alpha\gamma}(q)G_{\beta\delta}(-q)\left(\sum_{l_1} e^{i\vec{Q}\cdot\vec{r}^0(l_1)}\Lambda_\gamma(l_1)\right)\left(\sum_{l_2} e^{-i\vec{Q}\cdot\vec{r}^0(l_2)}\Lambda_\delta(l_2)\right) + \cdots$$

$$= \sum_{\substack{\alpha\beta \\ \gamma\delta}} Q_\alpha Q_\beta G_{\alpha\gamma}(q)G_{\beta\delta}(-q)\Lambda_\gamma(q)\Lambda_\delta(-q) + \cdots ,$$

where $G_{\alpha\beta}(q)$ is the Fourier transform of the lattice Green's function and is given by

$$G_{\alpha\beta}(q) = \sum_j \frac{e_\alpha(qj)e_\beta^*(qj)}{\omega_j^2(q)} ,$$

with j denoting phonon branches, and $\Lambda_\alpha(q) = \sum_l \Lambda_\alpha(l)e^{i\vec{q}\cdot\vec{r}^0(l)}$. Thus, we have

$$|F(Q)|^2 = \sum_{jj'} \frac{[\vec{Q}\cdot\vec{e}(\vec{q}j)][\vec{Q}\cdot\vec{e}(\vec{q}j')]}{\omega_j^2(q)\omega_{j'}^2(q)}$$

$$\times [\vec{e}(\vec{q}j)\cdot\vec{\Lambda}(\vec{q})][\vec{e}(\vec{q}j')\cdot\vec{\Lambda}(\vec{q})]^* + \cdots .$$

However, it can be shown that with q in principal symmetry directions of cubic crystals the factor $\vec{e}(\vec{q}, j)\cdot\Lambda(\vec{q})$ is nonzero only for the longitudinal branch $j = L$. Thus, for low impurity concentrations, we have

$$|F(\vec{Q})|^2 \sim c e^{-\alpha^2[\vec{e}(qL)\cdot\vec{Q}]^2}[\vec{Q}\cdot\vec{e}(\vec{q}L)]^2 W(\vec{q}),$$

with

$$W(q) = |\vec{e}(\vec{q}\cdot L)\cdot\vec{\Lambda}(\vec{q})|^2/\omega_L^4(q),$$

where c is the impurity concentration and the factor $e^{-\alpha^2[\vec{e}(\vec{q},L)\cdot\vec{Q}]^2}$ is to represent the effects of the higher-order terms in Δ in a fashion similar to the Debye-Waller factor for atomic vibrations.
rations.

[1] B. Borie, S. L. Sass, and A. Andreassen, Acta Crystallogr. A 29, 585 and 594 (1973).

[2] D. T. Keating and S. J. LaPlaca, J. Phys. Chem. Solids 35, 879 (1974).

[3] J. D. Axe, D. T. Keating, and S. C. Moss, Phys. Rev. Lett. 35, 530 (1975).

[4] B. M. Powell, P. Martel, and A. D. B. Woods, Phys. Rev. 171, 727 (1968).

[5] J. G. Traylor, N. Wakabayashi, and S. K. Sinha, Bull. Am. Phys. Soc. 20, 300 (1975); Solid State Div. Ann. Prog. Rep., 31 Dec. 1975, No. ORNL-5135 (unpublished), p. 111.

[6] S. S Chang and R. Collela, Phys. Rev. B 15, 1738 (1977). The neutron data quoted therein for Nb show a diffuse peak more intense than that found for Nb in the present work. The discrepancy may be due to the difference in the impurity, possibly oxygen, concentration.

[7] See, for example, W. Schmatz in *Treatise on Materials Science and Technology*, edited by Herbert Herman (Academic, New York, 1973), Vol. 2.

[8] The $1/\omega^4$ dependence of the distortion scattering was discussed by J. D. Axe and S. Shirane [Phys. Rev. B 8, 1695 (1973)] in their study of the central peak in Nb_3Sn.

[9] C. de Novion and W. Just, Annex to the Ann. Report 1976, Institut Laue-Langevin (unpublished), p. 288.

[10] H. G. Smith, Solid State Div. Ann. Prog. Rep., 31 Dec 1973, No. ORNL-4952 (unpublished), p. 91.